Molecular Foundry Example Proposal #3

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MOCVD and ALD Gallium Nitride for Surface Passivation of Gallium Arsenide PETE Cathodes

Facilities

Foundry Facilities

Facility	Description
Inorganic: *(lead)*	MOCVD system for GaN Growth, metal evaporator for metal surfactants, and wet chemistry labs for surface preparation
Fabrication: *(support)*	ALD growth of gallium nitride using GaCl3 and TMG precursors
ImagingManipulation: *(support)*	SEM with CL, Auger, and UV-PL

Proposal Description

Significance and Impact

We are pursuing a new method for solar energy harvesting based on an effect called Photon-Enhanced Thermionic Emission (PETE). In PETE, photons excite electrons from the valence band to the conduction band of a p-type semiconductor cathode (Fig. 1). These electrons then thermalize within the conduction band, and electrons which encounter the emissive surface with sufficient thermal energy can overcome the electron affinity and escape into vacuum ([redacted], et al., *Nature Materials* [redacted]).

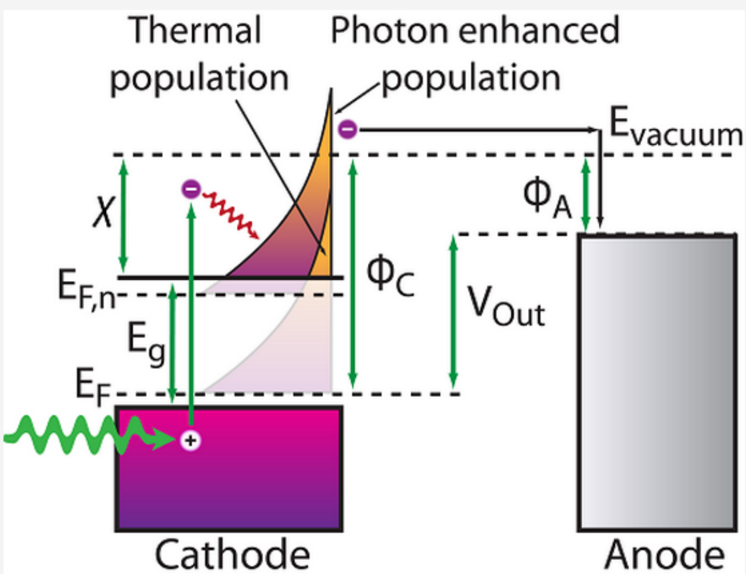

Fig. 1: Schematic diagram of a PETE converter.

To be relevant for energy conversion, a PETE cathode must have a high internal yield, i.e. a high ratio of emitted electrons to absorbed photons. We have demonstrated that a heterostructured cathode that combines an effective photon absorber with a wide-bandgap emitter would permit separate optimization of the bulk and surface properties of a PETE cathode (Fig. 3) ([redacted], et al., *Nature Comm.*, [redacted]). In the gallium arsenide/aluminum gallium arsenide system we explored in that work, the high absorption of gallium arsenide combined with the low interfacial recombination at the heterointerface dramatically improved the yield of the PETE process; however, the system was not thermally stable beyond ~120 degrees C. We are therefore seeking to develop a more stable, robust heterostructure cathode by growing ultra-thin layers of gallium nitride atop gallium arsenide substrates.

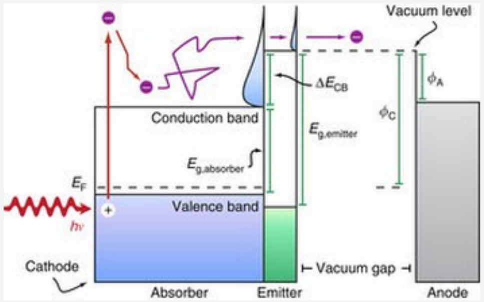

Fig. 2. Simplified view of a heterostructure PETE cathode

The ideal efficiencies of theoretical PETE converters are predicted to exceed those of photovoltaics (Fig. 3), as the PETE process can utilize the energy which is lost as heat in photovoltaic cells. However, these efficiencies demand low surface recombination velocity at the electron emission surface (Fig. 4).

If the surface recombination velocity of a GaAs cathode could be improved by even one order of magnitude by a GaN ALD coating and if the surface could be made temperature stable to 200 degrees C (80 degrees higher than the best device so far), the PETE yield from a bulk cathode could improve by as much as a factor of 20, and a thin-film cathode by even more still. In terms of technique development, the growth of ultra-thin seed layers of GaN by MOCVD and of thin films of GaN by ALD would be of utmost scientific interest, both to our application and more broadly for those working on high-power electronics and opto-electronic devices, where surface passivation and continuous seed layers for further film growth are active areas of research.

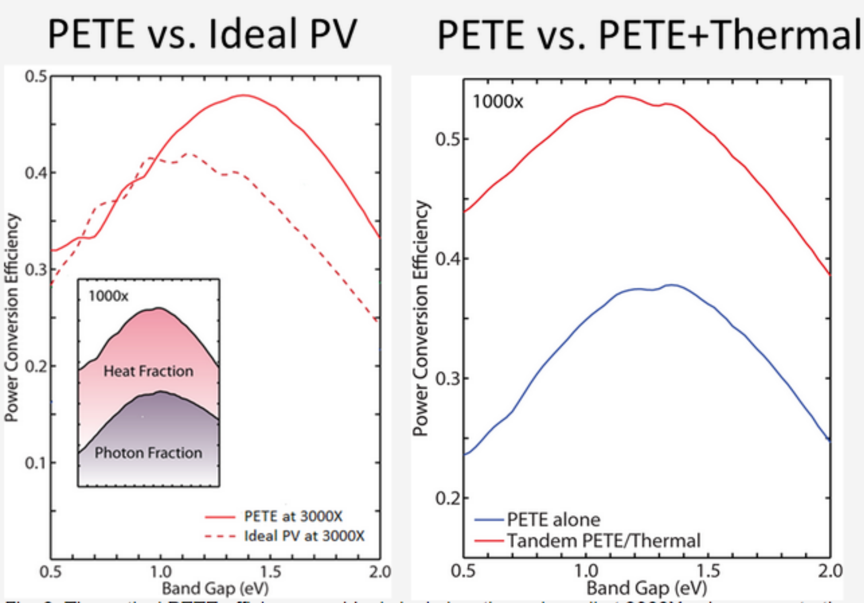

Fig. 3: Theoretical PETE efficiency vs. ideal single junction solar cell at 3000X solar concentration as a function of semiconductor bandgap

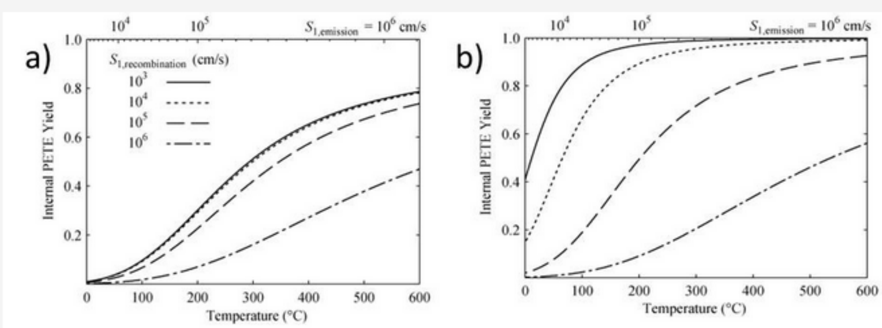

Fig. 4: Yield as a function of temperature and surface recombination velocity in a PETE cathode

Project Plan

Using the Molecular Foundry to grow new GaN/GaAs heterostructures by MOCVD and ALD would accelerate the development of the next generation of thermally stable PETE cathodes, complementing the test equipment development, anaytical and numerical simulation capacity, and nanostructing work we have been conducting at [redacted]

In our work over the past two years at the Molecular Foundry, we have focused on using MOCVD to grow gallium nitride layers on gallium arsenide substrates. We have experimented extensively on and presented results ([redacted], et al., ICNS Poster Presentation (2013)) from MOCVD growth of GaN under a variety of conditions: different crystallographic orientations of the GaAs substrate, growth temperatures, precursor gas composition and ratios, surface preparations, and surfactants (Fig. 5). We have substantially improved the chemical purity and rate of coalescence in the films we have grown over the time we have been using the facility, and we have also seen significant improvement in the photoluminescence intensity of the gallium arsenide substrate, indicating a reduced surface recombination velocity at the heterointerface (Fig. 6). However, electron emission from these heterostructured cathodes has been poor, likely because of substantial defects in the films resulting from the island growth mechanism of GaN in MOCVD. Researchers at the nitride semiconductor conference where we presented out work suggested a number of avenues for experimentation to induce smooth GaN growth, including magnesium surfactants, sulfur functionalization, and zinc oxide nanostructures; we plan to actively pursue these avenues and others as we continue our MOCVD work at the foundry.

The Molecular Foundry has recently begun growing titanium nitride by atomic layer deposition (ALD). Another aim of our project is to extend this system to develop the capacity to grow gallium nitride by ALD at the foundry using gallium chloride or trimethylgallium and ammonia precursors. ALD films of gallium nitride on gallium arsenide have been heretofore unexplored, but could offer a promising alternate path towards ultra-thin nitride films. First, it has been shown that ALD grown gallium nitride has little carbon incorporation and is self limiting over a wide temperature range of 180-350 degrees C (C. Ozgit et. al, J. Vac. Sci. Technol. A 30, 01A124 (2012)). The self-limiting behavior within the thermal stability window of gallium arsenide means that 2-dimensional growth instead of island growth may be possible, which could lead to much higher performance for our application. No ALD facility capable of growing this type of film exists at Stanford.

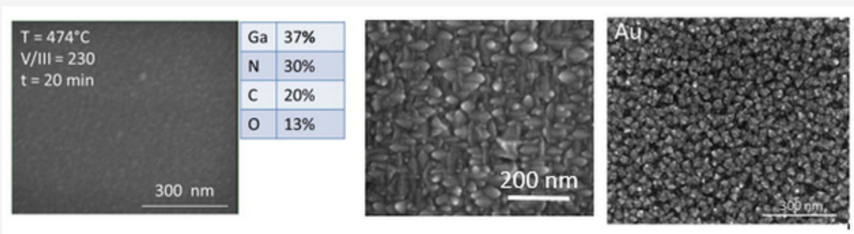

Fig. 5: From left to right: Continuous GaN film with high carbon incorporation using dimethyl hydrazine nitrogen precursor, polycrystalline GaN film using ammonia nitrogen precursor, and dense polycrystalline GaN film using evaporated gold surfactant layer.

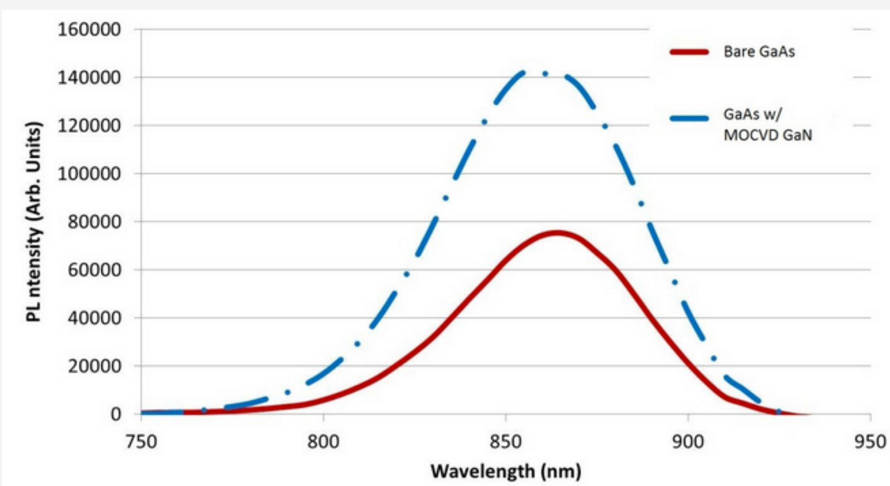

Fig. 6: Room temperature PL intensity as a function of wavelength for untreated GaAs and GaAs covered by an MOCVD-grown GaN film (film thickness ~ 10 nm).

After helping Foundry staff modify the ALD system to include gallium precursors, we will use planar (100) and (111)B GaAs substrates to determine the optimum temperature range, cycle times, and surface preparations for growing ultra-thin GaN layers by ALD. Characterization of these films by SEM, XPS, AES, and AFM will be very important, and we hope to use some of the Foundry's tools for this purpose.

In parallel with developments on planar cathodes, we have devised nanostructured cathodes based on Mie resonators which we have created through etching and selective area MOCVD of GaAs on [redacted] campus (Fig. 7). These nanostructures absorb light much more strongly than planar cathodes while offering crystallographically aligned surfaces for further epitaxial growth. Optimizing conformal growth around these nanostructures would be of utmost interest to simultaneously boost optical and electronic performance of this class of PETE cathodes. Developing a technique to deposit thin, continuous passivation layers is more broadly applicable to all nanostructured solar cells, where interfacial recombination often mitigates the light trapping benefits arising from the nanostructures ([redacted], *Nanophotonics*, [redacted]).

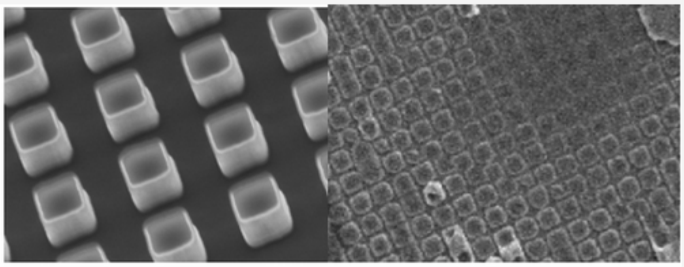

Fig. 7. Gallium arsenide nanostructures fabricated by plasma etching and passivated by ALD alumina (left) and selective area MOCVD (right). Pattern pitch = 500 nm.

Molecular Foundry Utilization Timeline

We intend to visit the foundry twice per week on average for one year from May 2014-May 2015:once per week for growth, and once per week for characterization. [redacted], the primary researcher, is already an independent user of the MOCVD system and the SEM suite and will not require additional training beyond that required for use of the ALD system.

MOCVD
May 2014-May 2015 - Experimentation with magnesium surfactants, sulfur surface functionalizations, and zinc oxide nanowaffle structures to promote smooth gallium nitride seed layers by MOCVD. The substrates to be used will include planar (100), planar (311)B (high step density for accelerated nucleation), and nanostructured (111)B.

ALD
July-September 2014:
Installation of GaCl3 and TMG ALD sources, characterization of calibration films on sapphire and GaN MOCVD substrates by XRD, XPS, and AFM to determine crystallinity and chemical purity of grown films.

October-December 2014: Optimization of growth temperature, cycle times, and surface preparation for GaN ALD on planar (100) GaAs.

January 2015-May 2015- Optimization of growth temperature, cycle times, and surface preparation for conformal GaN ALD on GaAs (111)B basal plane nanostructures.

After characterizing the samples grown by MOCVD and ALD ex-situ at the Foundry, we will perform photoemission measurements on them using our ultra-high vacuum photoemission test chamber at [redacted] to determine the thermal and temporal stability of the films.   We also have the capability to do scanning photoluminescence and kelvin-probe spectroscopy, which could prove very useful for determining the homogeneity of the GaN films on the nanostructured GaAs photocathodes.

Relevant Experience

The primary researcher, [redacted] has been an active user of the Foundry's two gallium nitride MOCVD systems over the past two years, as well as the SEM suite (with CL) and the wet labs on the 4th floor. He has gained proficiency in both MOCVD growth and characterization of GaN and GaAs films at Stanford at LBL by SEM, XPS, Auger, XRD, and other techniques. He also is experienced in depositing ALD films (alumina) as a passivation layer on GaAs devices. [redacted] has been a co-author on a number of high impact publications in the field of nanoscale fabrication (see http://www.[redacted]) and been an invited contributor to journals and conferences in the fields of optics and photonics.

The co-researchers, [redacted] and [redacted], have been working on PETE for more than five years and are subject experts on photoemission and thermionic emission from III-V materials. [redacted] has authored three high impact papers on PETE in Nature Materials, Nature Communications, and the Journal of Applied Physics.

Need for the Molecular Foundry

The availability of GaN MOCVD and ALD systems for nitride growth combined with the Foundry staff's extensive experience growing nitride semiconductors will greatly accelerate progress on this project. No such systems are currently available at [redacted]. Continued access to the SEM suite (with cathodoluminescence capabilities) and the Auger Electron Spectroscopy system will also be valuable to quickly iterate through growth parameters and monitor morphology of grown films over the coming year.